

Chemical Considerations for the Selection of the Coolant for
the Advanced High-Temperature Reactor

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Chemical Considerations for the Selection of the Coolant for the Advanced High-Temperature Reactor

1. Scope

The purpose of this report is to provide an assessment of key chemical factors related to the choice of the primary coolant for the Advanced High-Temperature Reactor (AHTR). The most important chemical factor in this selection concerns the maintenance of acceptably small levels of corrosion for the metal alloy that will serve as primary containment. Alloy corrosion is the key materials-compatibility issue that is influenced by salt chemistry.

A review of properties of candidate AHTR coolants has already been conducted,¹ and a list of potential candidate salts derived from this study is listed in Table 1.

Table 1. Useful Low-Freezing Salt Compositions for AHTR Coolants

<i>Alkali Fluorides</i>	<i>ZrF₄ – salts</i>	<i>BeF₂ – salts</i>
	LiF-ZrF₄ (51-49) 509°C	
	NaF-ZrF₄ (59.5-40.5) 500°C	
LiF-KF (50-50) 492°C		
LiF-RbF (44-56) 470°C		
LiF-NaF-KF (46.5-11.5-42) 454°C		LiF-BeF₂ (67-33) 460°C
LiF-NaF-RbF (42-6-52) 435°C	LiF-NaF-ZrF ₄ (26-37-37) 436°C	LiF-BeF ₂ -ZrF ₄ (64.5-30.5-5) 428°C
	RbF-ZrF₄ (58-42) 410°C (52-48) 390°C	
	KF-ZrF₄ (58-42) 390°C	
		NaF-BeF₂ (57-43) 340°C
		LiF-NaF-BeF ₂ (31-31-38) 315°C

2. Introduction

The application of molten salt coolants is based on a 50-year history of molten salt nuclear technology, principally at the Oak Ridge National Laboratory (ORNL). In order to appreciate the merits of using such high-temperature condensed fluids as coolants in AHTRs, it is worthwhile to review some of that history as it pertains to AHTR applications. Although many more-extensive reviews of molten salt reactors exist, these might be too expansive in scope for those interested only in specific topics such as those of concern in AHTR technology. Therefore, in this introduction, key aspects will be cited in the development of these very unique high-temperature fluids as they pertain to AHTRs. This report will then focus in detail on these key elements that will lead to consideration of molten salt coolants for further development.

The use of molten salts in nuclear reactors has been an evolutionary process that included the parallel development of containment materials, physics, engineering, etc. Necessarily, this broad effort required the commitment of a large number of scientists and engineers over at least three decades. It is worth emphasizing that the use of molten salts was not originally envisioned but instead appeared as part of the evolutionary process to meet design requirements.

2.1 Aircraft Nuclear Propulsion (ANP) Project

In the 1950s, a nuclear-powered strategic bomber was conceived that could stay aloft for more than a month and be diverted to a target should the necessity arise in this era of the Cold War. To power such an aircraft, a test reactor—the Aircraft Reactor Experiment (ARE)—was constructed. A major requirement for this reactor was that it have a very high power density in order to keep the weight in the aircraft at a minimum. Originally, a more conventional design of solid fuel pins with liquid metal (sodium) was planned. However, the need for the high power density and safety could not be met with solid fuel, which might be inadequately cooled in such a design.

Therefore, it was decided to develop a liquid fuel that could operate at a high power density and that was inherently safe because of a negative power coefficient. In other words, if the reactor power went up excessively, the thermal expansion of the fluid fuel would cause a natural lowering of the amount of fuel in the core and thus decrease the overall reactor power. A search then began for a high-temperature fluid that would satisfy the following requirements:²

1. Consist of elements of low-neutron-capture cross section.
2. Dissolve more than the critical concentration of fissionable material at temperatures safely below the temperature at which the fuel leaves the heat exchanger.
3. Be thermally stable with low vapor pressure over the operating temperature range.

4. Possess heat transfer and hydrodynamic properties adequate for its service as a heat-exchange fluid.
5. Be relatively nonaggressive toward some otherwise suitable material of construction, presumably a metal, and toward some moderator material.
6. Be stable toward reactor radiation and be able to survive fission of the uranium or other fissionable material. Must tolerate fission-product accumulation without serious deterioration of its useful properties.
7. Be relatively inexpensive and capable of an economical reprocessing scheme.

Various inorganic compounds such as halides, nitrates, hydroxides, and carbonates were considered, and many of these were tested in the laboratory, primarily for corrosive action on potential container materials. Of these many classes of inorganic compounds, fluorides were deemed much more suitable, for reasons that include improved neutron economy, better moderating efficiency, higher chemical stability, lower vapor pressure, higher specific heat, and usefulness of the element without isotope separation.³

For the ARE, a mixture of NaF and ZrF₄ was used as the fluoride solvent⁴ for the UF₄ fuel component to make a solution of NaF-ZrF₄-UF₄ (53.09-40.73-6.18 mol %). The containment metal used for this liquid fuel mixture was a nickel-base alloy, Inconel, (15% Cr, 7% Fe, balance Ni).⁵ Although it was initially planned to use a sodium-cooled, solid-fuel-element reactor, the reactor design evolved first to that of a sodium-cooled, stationary-liquid-fuel reactor and, finally, to that of a circulating-fuel reactor employing sodium as a reflector coolant.⁴ The ARE operated in November 1954 for 221 h at a maximum power of 2.5 MW.

Postoperative examination of the reactor components plus experimental corrosion-loop testing revealed that Inconel corrosion was excessive for long-term operation but could be improved by modifying the alloy through the addition of molybdenum. Furthermore, corrosion loops indicated that Inconel was more severely corroded with fuel salts made with all alkali-metal fluorides than those made with NaF-ZrF₄ mixtures, suggesting that the chemical composition of the fuel salt played a significant controlling role in the corrosion chemistry. Extensive development in materials research⁶⁻¹⁰ resulted in the production of an improved nickel-base alloy, INOR-8 (17% Mo, 7% Cr, 5% Fe, balance Ni).

The period following the successful operation of the ARE evolved to the design and prototype construction of an Aircraft Reactor Test (ART). The work progressed with further development and testing until the Atomic Energy Commission terminated the ANP project in 1957.¹¹ This novel molten salt technology was then turned to civilian interests in the development of molten salt breeder reactors with the design and construction of the Molten Salt Reactor Experiment (MSRE).

2.2 Molten Salt Reactor Experiment

The MSRE represented the first step in developing a breeder reactor. To this end, it was necessary that the molten solvent components consist of elements with especially low thermal neutron cross sections in order to achieve the highest possible breeding ratio in the breeder reactor prototype.¹² The MSRE was planned to test the combination of new components and the overall reactor design—without including the breeding stage. It was constructed of INOR-8 (now identified as Hastelloy N) for improved corrosion resistance and fueled with LiF-BeF₂-ZrF₄-UF₄ (64-30-5-1 mol %). The LiF component was enriched Li-7 for better neutron economy. Neutron moderator graphite filled the reactor core in the shape of rectangular stringers that provided channels for the circulating fuel. The fuel was circulated from the reactor core at 650°C to a heat exchanger operating at 550°C.

Corrosion in the reactor circuit was controlled by reducing approximately 1% of the UF₄ solute to UF₃, so that the oxidative equilibrium between the chromium of the Hastelloy N container was shifted to the left:



Postoperative examination of the reactor container showed that corrosion was successfully minimized by this redox method of control. Perhaps it would be useful to say that the fuel salt produced only very minor, and barely detectable levels of corrosion, whereas for the coolant salt the corrosion was not detected at all.

Further postoperative examination showed that fission-product tellurium diffused into the Hastelloy N grain boundaries and caused an unacceptable stress-cracking embrittlement of the metal. Radiation hardening of the Hastelloy N and diffusion of tritium (which was produced by the action of the neutrons on the lithium component of the solvent) were also of concern for future reactor applications.

2.3 Molten Salt Breeder Reactor (MSBR)

In 1972, following the success of the MSRE operations and encouraging R&D solutions to the postoperative findings, the next step in development was to move toward a breeder reactor.¹³ However, competition with the broad Liquid Metal Fast Breeder Reactor (LMFBR) program curtailed further extensive progress. Nevertheless, significant developments in two areas of interest are worthy of recognition: materials and fuel salt chemistry.

This historical introduction covering the development of molten salt technology over a period of several decades should demonstrate how various aspects evolved. The selection of an appropriate molten salt medium and the effects on the container material (corrosion) are the two subjects of focus in this report. They will be discussed separately with recommendations, as appropriate, for application to coolant technology.

3. Materials for High-Temperature Fluids

Inconel was originally found to be superior to non-nickel-base alloys and therefore used in the ARE. However, the extent of corrosion was still found to be excessive for prolonged reactor operations. As a result, an alloy development program was initiated based on the encouraging results found with Inconel.⁹ Studies were started¹⁹ on the Ni-Mo system, which exhibited excellent corrosion properties both from the standpoint of measurements of equilibrium solubilities on various metals in salt mixtures and on the basis of tests that were made with the commercial alloy Hastelloy B (composition: 29% Mo, 5% Fe, balance Ni). Corrosion rates for this alloy were seen to be quite low at temperatures in excess of 900°C and very much lower than those for Inconel under comparable conditions. However, Hastelloy B suffered from several adverse characteristics. Of these, poor fabricability and embrittlement after operation between 650 and 815°C, coupled with poor oxidation resistance at elevated temperatures, qualified its good performance in the area of corrosion rate.

In developing an improved nickel-base alloy for long-term operation as a molten fluoride container, when varying the amount of chromium, it was found that a significant change in the oxidation rate* occurs at about 6% Cr. At this composition, the oxide changes from the NiMoO₄ type to one that is predominantly the Cr₂O₃ type.¹⁴ Since a high chromium content is undesirable from the standpoint of fused fluoride corrosion, only a slight excess of chromium is desired for the proposed alloy. Molybdenum, which strengthens nickel alloys, was reduced in amount to the point that a solid solution of nickel and molybdenum would be stable at all temperatures of interest.

On the basis of extensive testing, an alloy that was designated as INOR-8 (now identified as Hastelloy N with composition 17% Mo, 7% Cr, and 5% Fe, balance Ni) was selected as the most promising container material for fused fluorides. Interestingly, the iron content was included so that the chromium may be added as ferrochromium rather than pure chromium with the resulting decrease in costs. This alloy served the operation of the MSRE in an excellent fashion, and it was only after reactor operations that some deficiencies were observed.

As stated in Sect. 2.2, postoperative examination of the MSRE revealed the damaging effects of fission-product tellurium, resulting in the development and testing of modified alloys for future containment purposes. It was found that additions of titanium or niobium produced a modified Hastelloy N alloy that had good resistance to both radiation embrittlement and to intergranular cracking by tellurium.^{15,16} Furthermore, it was seen that the control of the molten salt oxidation potential had dramatic effects on the extent of cracking¹⁷ as shown in Figure 1. This technique of salt chemistry control by redox changes, which was performed during the operation of the MSRE and was known

* "Oxidation" as opposed to "corrosion", realizing that the other side of the container is exposed to the atmospheric environment.

even before then as a technique for preventing corrosion of all metal alloys, is clearly one of the best means of containment corrosion control. Redox control plus prudent selection of components for the coolant salt mixture is at the core of the recommendations for AHTR molten salt coolant design.

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EXTENT OF TELLURIUM EMBRITTLEMENT OF HASTELLOY N
IS STRONGLY AFFECTED BY OXIDATION POTENTIAL OF SALT.

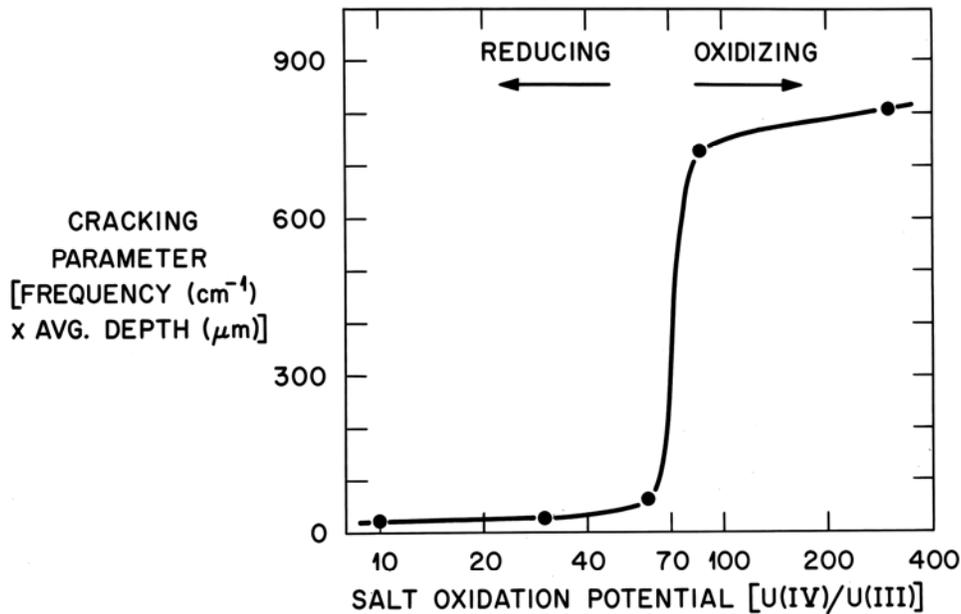


Fig. 1. Effect of redox potential on tellurium cracking of Hastelloy N.

4. Chemistry of Molten Fluoride Salt Coolants

The selection and effective use of molten salts as high-temperature coolants is dependent on an understanding of the chemistry. Of major importance in this understanding are: (1) the ability to produce and maintain a high level of purity, (2) phase diagram behavior for mixtures, (3) the utilization of acid-base effects, and (4) the control of the redox potential of the salt medium as it affects corrosion and other chemical processes.

4.1 Salt Purification

Molten salt use typically begins with the acquisition of raw components that are combined to produce a melt mixture that has the desired properties when melted. However, most suppliers of halide salts do not provide materials that can be used directly. The major impurities that must be removed are moisture/oxide contaminants, to prevent severe corrosion of the container metal. Once removed, these salts must be kept from atmospheric contamination by handling and storage in sealed containers. During the ANP/MSRE era, a considerable effort was devoted to salt purification by HF/H₂ sparging of the molten salt and is described in numerous reports.^{3,9,18,19,20} Besides removing moisture/oxide impurities, the purification also removes other halide contaminants, such as chloride, plus sulfur. The sulfur is usually present in the form of sulfate and is reduced to sulfide ion, which is swept out as H₂S in the sparging operation. Methods were also developed to insure the purity of the reagents used to purify the salts, and to clean the container surfaces used for corrosion testing.

Another means of purification that can be incorporated following the sparging treatment involves simply reducing the salt with an active metal such as the alkali halides, zirconium, etc. While such active metals will remove oxidizing impurities such as HF, moisture, or hydroxide, they will not affect the other halide contaminants that effect sulfur removal. Therefore, it seems inevitable that the HF/H₂ sparging operation either by itself or followed by active metal treatment, will be a necessity.

Although a great deal of effort can be devoted to purifying the molten salt mixture in the manner described above, it is primarily useful in producing materials for research purposes without the possibility of interference from extraneous impurities. In the final application of molten salts, one can envision that a less strenuous and less expensive purification treatment might suffice for high-temperature-coolant purposes.

4.2 Phase-Diagram Behavior

Salt components by themselves often have melting points and/or other properties that preclude their use. For example, the alkali fluorides individually have melting points in excess of 800°C, which make them difficult to use alone as a liquid medium. However, the combination of two or more of these component salts can produce low-melting mixtures that satisfy the melting point requirements of a system. Furthermore, some properties of individual components, such as viscosity (for pure BeF₂) or vapor pressure (for pure ZrF₄), are reduced along with the resulting melting point by combination with other salt components. For these reasons, a large effort had been devoted to the study of phase diagrams for various mixtures of fluoride salts.

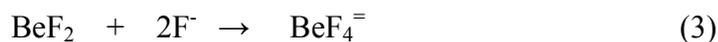
While many combinations are documented in various references,^{3,21} it is conceivable that the phase diagram of some salt mixture for high-temperature-coolant applications has not been reported and must be determined.

4.3 Acid-Base Chemistry

A less obvious but equally important chemical aspect is that of the molten-salt acid-base chemistry. To put it in proper perspective, one should realize that an aqueous chemical process would never be developed without control of the acid-base properties of the solution, because most chemical processes simply do not work well without such control of the solutions. Similarly, this control can be essential in molten salt chemistry. The major obstacle in understanding the acidity effect is in comprehending the nature of this Lewis acid-base property, in which an acid is defined as an electron pair acceptor and a base as an electron pair donor. For molten fluorides, ZrF_4 , UF_4 , and BeF_2 would be examples of Lewis acids. These acids would interact with a Lewis base, F^- , in the following fashion:



Salts that easily give up their fluoride ions—the alkali metal fluorides—interact with the acidic salts that accept them to form complexes as shown above. The effect of such complexation is a stabilization of the acidic component and a decrease in the chemical (thermodynamic) activity. Although these concepts were realized in the early development stages of molten salt chemistry, a more macroscopic (thermodynamic) view of solvent changes was taken and resulted in the laborious measurement of activity coefficients for individual components in specific salt mixtures. A classic presentation²² of activity coefficients for numerous fluoride salts (Fig. 2) as a function of increasing LiF content (i.e., increasing basicity) in the LiF - BeF_2 mixtures formed the basis for much of the understanding of that time. It was invaluable for predictions of equilibrium concentrations of reactive components in these solutions. Prior to that, there were such suggestive observations¹² that corrosion of Inconel was much worse with the ternary alkali metal fluoride eutectic (a basic salt solution) than with NaF - ZrF_4 (acidic salt solution) containing UF_4 . We now explain this as being due to an increase in the stability of the corrosion product by complexation with the higher activity of the fluoride ions in the basic salt mixture. Such acid-base properties are also seen in the viscosity decrease of acidic BeF_2 (viscous because of cross-linking through a Be - F - Be bridging network) with additions of the basic component F^- to form monomeric $\text{BeF}_4^{=}$ ions of normal solution viscosity (~ 1 – 10 cp):



Acid-base effects are also seen in vapor pressure changes of volatile ZrF_4 to form the nonvolatile $\text{ZrF}_6^{=}$ ion:



Today, the understanding of the more microscopic coordination chemistry of these systems through the use of various spectroscopies that can identify the coordination behavior of the ions enables a prediction of these chemical equilibrium shifts, at least on a qualitative scale. Acid-base chemistry then becomes an essential factor in the selection of components for high-temperature coolants.

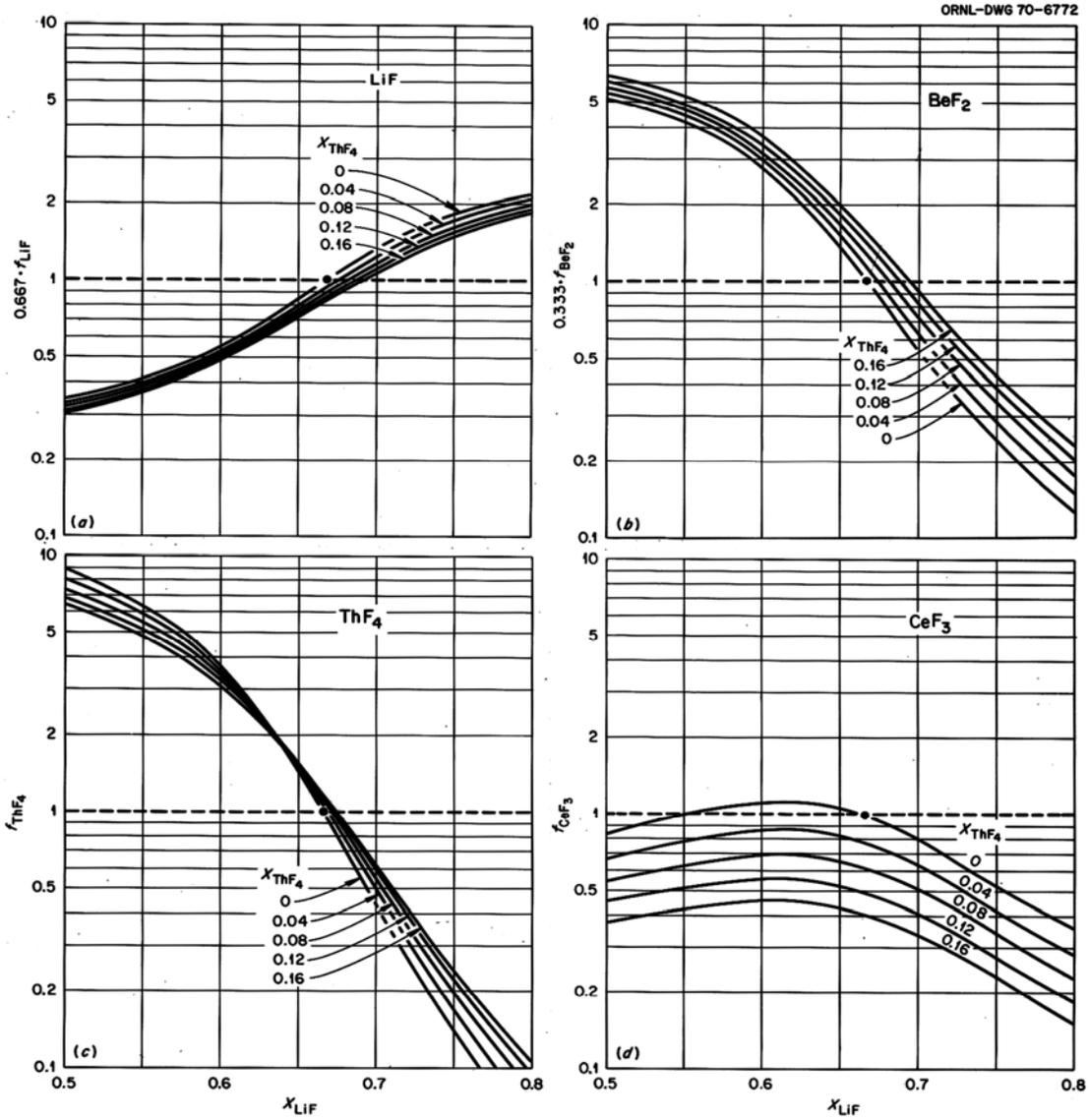


Fig. 2. Activity coefficients of various components versus LiF content (as mole fraction) showing acid-base effects on metal ions in solution. Standard state is 2LiF-BeF₂.

4.4 Corrosion Chemistry

Corrosion has long been a major problem in the use of metals and is a major concern in using such materials for containment purposes. Consequently, years of study have been devoted to corrosion chemistry in various media, but especially in aqueous solutions. Indeed, this same concern has prevailed for metallic containment of molten salts and was actively pursued throughout the years of development.

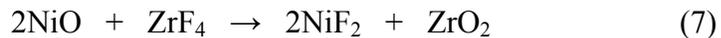
Unlike the more conventional oxidizing media, the products of oxidation of metals by fluoride melts tend to be completely soluble in the corroding media¹⁴; hence, passivation is precluded and corrosion depends directly on the thermodynamic driving force of the corrosion reactions.⁷ Design of a chemically stable system utilizing molten fluoride salts, therefore, demands the selection of salt constituents that are not appreciably reduced by available structural metals and the development of containers whose components are in near thermodynamic equilibrium with the salt medium.

Examination of the free energies of formation for the various alloy components in Inconel or Hastelloy N shows that chromium is the most active of the metal components. Therefore, any oxidative attachment to these nickel-base alloys should be expected to show selective attack on the chromium. Such oxidation and selective attack follow from reactions such as the following² for the fuel salt:

Impurities in the melt with dissolution of the CrF₂



Oxide films on the metal



These reactions are followed by reaction of NiF₂ with Cr:

Reduction of UF₄ to UF₃



Of course, in the case of a coolant salt with no fuel component, reaction (8) would not be a factor.

Redox processes that are responsible for attack by molten fluoride mixtures on these alloys result in selective oxidation of the contained chromium. This removal of chromium from the alloy occurs primarily in regions of highest temperature and results in the formation of discrete voids in the alloy.²³ These voids are not, in general, confined to the grain boundaries in the metal but are relatively uniformly distributed throughout the

alloy surface that is in contact with the melt. The rate of corrosion has been measured and was found to be controlled by the rate at which chromium diffuses to the surfaces undergoing attack.⁹

5. Coolant Salt Selection Factors Related to Corrosion

From the list of potential coolant salts, there are none that are intrinsically corrosive to the metal alloy components. This view is based on the thermodynamic stability of the fluoride components relative to those of the alloy metal is described in depth by Grimes² and summarized in the Corrosion Chemistry section, above. Furthermore, it has been demonstrated over the past several decades in systems operating up to 850°C.

Nevertheless, the evidence for making a selection of coolant based on corrosion is not adequate at present. Previous studies focused on the corrosion by salts containing uranium, in which the presence of uranium is the key factor in the intensity and nature of alloy corrosion [cf., Eq. (8)]. A good understanding of fuel salt corrosion was developed, but we do not know the precise mechanism of persistent (i.e., mass-transfer) corrosion of nickel alloys with coolant salts. We must assume that redox-sensitive species, such as Cr(II/III) and Fe(II/III), are important factors in this process. However, with limited analytical resources, other factors apparently present in previous studies must be evaluated to identify all truly significant trends.

5.1 Oxidation State of Corrosion Products

During the ANP program, a continuing effort was made to understand the oxidation state of corrosion products such as Cr, Fe, and Ni in different salts. Although these studies were crude by today's standards, the basic trends of oxidation state stability, shown in Table 2, were apparent and helped explain the corrosion phenomena that were being observed in fuel salts.

FLiNaK	Cr(III)	Fe(II/III)	Ni(II)
NaF/ZrF ₄	Cr(II)	Fe(II)	Ni(II)
2LiF/BeF ₂	Cr(II)	Fe(II)	Ni(II)

It is apparent that FLiNaK has a distinct behavior. As a strongly basic solvent, it would tend to stabilize the M(III) oxidation state and could provide for a stronger corrosion driving force due to the variation between cation [Cr(II/III), Fe(II/III)] oxidation states with temperature.

5.2 Temperature Dependence of Dissolved Chromium Concentration

The equilibrium level of dissolved chromium has been measured for fuel salts, but not for coolant salts. Although the information on fuel salts is not directly applicable to coolants, we expect that fuel systems that experience minimal corrosion would also be better coolants. Review of the dissolved chromium levels for various fuel salts in Table 3 again reveals that FLiNaK stands somewhat apart from the other salts as supporting a higher degree of corrosion. It also appears that there is some benefit in avoiding a very acid (high-ZrF₄ or BeF₂-content) system and that a salt mixture that has a nearly complete coordination shell (2:1 ratio of alkali halide to Zr or Be, and heavier alkali salt) has the least potential for supporting corrosion based on the temperature sensitivities shown in Table 3.

Table 3. Equilibrium Level of Dissolved Metals for Pure Elements in Contact with Various Fuel Salts

Salt Mixture	Mol % ZrF ₄ or BeF ₂	[UF ₄] mol %	[Cr] at 600°C	[Cr] at 800°C
FLiNaK	0	2.5	1100	2700
LiF-ZrF ₄	48	4.0	2900	3900
NaF-ZrF ₄	50	4.1	2300	2550
NaF-ZrF ₄	47	4.0	1700	2100
NaF-ZrF ₄	41	3.7	975	1050
KF-ZrF ₄	48	3.9	1080	1160
NaF-LiF-ZrF ₄ (22-55-23)	23	2.5	550	750
LiF-BeF ₂	48	1.5	1470a	2260
LiF-BeF ₂	?	?		

This approach is a significant oversimplification, as the identify of the various species is very important. For example, the saturating species that contains chromium is different for each of these salts. However, to a first approximation, this table is a useful guide.

5.3 Polythermal Corrosion Test Loops with Coolant Salts

Although less than 10% of all corrosion testing was done with salts that were free of uranium, this small fraction amounts to a significant body of work because of the extensive test program that was carried out. The results of testing for uranium-free salts are summarized in Table A.1 in the Appendix.

A quick inspection of this table reveals that Hastelloy-N (INOR-8) is a superior choice (rather than Inconel or SS) for coolant salts, as it is for fuel salts. The corrosion is so intense and the duration so short for most Inconel loops that it is hard to make a judgment about which salt supports the least corrosion. It is clear that FLiNaK is certainly among the worst. For INOR-8 loops, the corrosion is so minor that it is hard to sort out corrosion effects due to the composition of the salt. Some additional Inconel loop tests^{24,25} were

conducted with special fuel salt mixtures in which the ZrF_4 and BeF_2 concentrations were varied in an attempt to select the best composition. However, these tests were somewhat inconclusive because of the short test duration (500 h) and the impurity effects. Within the resolution of these tests, the trends indicated in Table 3 were verified: very basic (FLiNaK) and very acidic ($LiF-ZrF_4$) salts showed the worst performance. *Nevertheless, the proper control of redox factors, as described below, can make even these salt mixtures acceptable with respect to corrosion.*

5.4 Redox Control Factors

At various periods at ORNL, the control of the oxidation-reduction state of the salt was explored as a means to minimize corrosion. During the ANP period, this approach was found to be somewhat effective. However, it was not practical, because strong reductants either reduced zirconium or uranium in the salt to a metal that plated on the alloy wall or resulted in some other undesirable phase segregation. During the MSRE operation, periodic adjustment of the U(III)/U(IV) ratio was effective in limiting the corrosion in the fuel circuit. Keiser also explored the possibility of using metallic beryllium to reduce corrosion in stainless steel containing a $2LiF-BeF_2$ salt.²⁶ This treatment was effective only as long as the solid beryllium was immersed in the salt. There was little, if any, buffering capacity in this salt to maintain the reducing environment throughout the melt. Del Cul et al. have identified and tested candidate agents that could be used as redox buffers to maintain a reducing environment in the coolant circuit.²⁷

None of these redox-control strategies have been developed to the extent that we can rely on them for a definite salt selection. However, we can make some useful observations in this regard. For a lower-temperature system ($<750^\circ C$), it appears that Hastelloy-N is fully capable of serving as a containment alloy without the need for a sophisticated redox strategy. Even a salt like FLiNaK could be suitable.

For temperatures in excess of $750^\circ C$ and for alloys that will contain more chromium (as most higher-temperature alloys do), it appears that a reducing salt will be needed to minimize corrosion. Inconel without the benefit of a reducing environment was found to be unsuitable for long-term use. Only a mildly reducing environment is possible with a ZrF_4 -containing salt since a strongly reducing redox potential would reduce ZrF_4 , itself. Much more reducing systems can be devised with either FLiNaK or BeF_2 salts. Some very important material compatibility issues will have to be explored in order to use a highly reducing salt at these higher temperatures, because heretofore unmentioned events such as carbide formation and carburization/decarburization of the alloy become a significant threat.

Should low-chromium/chromium-free alloys or suitable clad systems be devised as a container then these problems with salt selection will largely disappear.

However, in the absence of this solution, it appears that two types of strategies exist: (1) select a salt that supports corrosion the least and does not require that a highly reducing environment be maintained (some ZrF_4 salts, FLIBE) or (2) select a salt with a

large redox window that can be maintained in a highly reducing state (FLiNaK, FLIBE). Given the expense and difficulty of doing development work with beryllium-containing salts, it seems logical to explore the most promising ZrF₄ salts without strong reductants and to explore FLiNaK with strong reductants and/or redox buffers.

6. Recommendations

The selection of a suitable coolant salt should be based on numerous factors, including chemical, physical, nuclear, metallurgical, and economic factors. It is evident from the past decades of experience that fluoride melts have an established advantage over the few other coolants that had been considered previously for extreme-temperature service (>700°C). The following remarks are directed primarily toward selection based on chemical factors that relate to corrosion, with the understanding that the overall assessment will need to account for other factors.

Proper selection of a coolant salt based on chemical differences is based largely on the acid-base properties of the combination, as described above. Both predictions and measurement of the container-metal-fluoride equilibrium concentrations are higher in basic salts as compared with neutral or acidic media. Some corrosion loop experience tends to corroborate this observation. However, unfortunately, no systematic study of such a phenomenon has been made during these experiments.

A neutral or slightly acidic salt melt would be predicted to be the most advantageous with respect to corrosion behavior. However, basic salt melts tend to have significantly lower vapor pressures and lower viscosities, and these properties might present a problem (e.g., ZrF₄ and BeF₂). Therefore, any selection of a coolant based on chemical considerations must, necessarily, be a compromise of all factors that might affect performance.

In this regard, it is recommended that two types of salts should be studied in the future, and the following selections are made:

- (1) Salts that have been shown in the past to support the least corrosion and are neither strong Lewis acids nor strong Lewis bases (i.e., “neutral”). The salts BeF₂ and ZrF₄ in the concentration range of 30–35 mol % of ZrF₄/BeF₂ fall into this category.
- (2) Salts that provide the most opportunity for controlling corrosion by establishing a very reducing salt environment. The alkali-halide (FLiNaK, FLiNaRb) salts and the BeF₂-containing salts fall into this category.

In addition, it is recommended that alkali-halide and ZrF₄-containing salts be investigated first because of the difficulty and expense of work with BeF₂. It is likely that much of what we need to learn for work at temperatures above 750°C can be gathered initially, before actually working with BeF₂.

7. References

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Appendix

Table A.1. Summary of Corrosion Testing Results for Salts without Uranium

Loop #	Alloy	Salt	Duration, h	Peak, °C	Corrosion, mil
116	316SS	FLiNaK	500	815	4
119	316SS	FLiNaK + NaK	500	815	2
347	Inconel	50NaF-50ZrF ₄	3000	815	11
518	Inconel	NaF-ZrF ₄	3000	815	11
346	Inconel	50NaF-50ZrF ₄	2000	815	9
519	Inconel	NaF-ZrF ₄	2000	815	12.5
78	Inconel	FLiNaK	1000	815	13
	Inconel	NaF-ZrF ₄	1000	815	3
278	Inconel	NaF-ZrF ₄	1000	815	5
399	Inconel	NaF-ZrF ₄	1000	815	10
	Inconel	60NaF-40ZrF ₄	1000	815	5
	Inconel	50NaF-50Be ₂	1000	815	8
	Inconel	70NaF-30BeF ₂	1000	815	6
	Inconel	24LiF-53NaF-23BeF ₂	1000	815	5
	Inconel	36LiF-49NaF-15BeF ₂	1000	815	3
	Inconel	74LiF-26ThF ₄	1000	815	6
517	Inconel	NaF-ZrF ₄	822	815	5.5
337	Inconel	NaF-ZrF ₄	575	815	8
214	Inconel	FLiNaK + NaK	500	815	3
230	Inconel	36NaF-18KF-46ZrF ₄	500	815	10
348	Inconel	50NaF-50ZrF ₄	500	815	5.5
	Inconel	FLiNaK	500	815	7
934	Inconel	60NaF-40ZrF ₄	500	815	5
935	Inconel	60NaF-40ZrF ₄	500	815	5
	Inconel	NaF-BeF ₂	500	815	10
	Inconel	LiF-NaF-BeF ₂	500	815	5
246	Inconel	52NaF-48ZrF ₄	500	815	8
262	Inconel	57NaF-43BeF ₂	500	815	9
277	Inconel	50NaF-50ZrF ₄	500	815	5

Loop #	Alloy	Salt	Duration, h	Peak, °C	Corrosion, mil
276	Inconel	NaF-ZrF ₄	500	815	8
277	Inconel	NaF-ZrF ₄	500	815	4
336	Inconel	NaF-ZrF ₄	500	815	6
341	Inconel	NaF-ZrF ₄	500	815	5.5
342	Inconel	NaF-ZrF ₄	500	815	6
516	Inconel	NaF-ZrF ₄	500	815	6
338	Inconel	NaF-ZrF ₄	500	815	6
411	Inconel	NaF-ZrF ₄	250	815	4.5
410	Inconel	NaF-ZrF ₄	100	815	4
400	Inconel	NaF-ZrF ₄	50	815	3
1181	Inconel	71LiF-29ThF ₄	8760	732	6.5
1239	Inconel	71LiF-16BeF ₂ -13ThF ₄	8760	732	7.5
9377-6	Inconel	71LiF-16BeF ₂ -13ThF ₄	13155	704	13
1188	Inconel	35LiF-27NaF-38BeF ₂	8760	677	9
1210	Inconel	71LiF-29ThF ₄	8760	677	5
1235	Inconel	71LiF-16BeF ₂ -13ThF ₄	7789	677	4
1214	Inconel	FLiNaK	4673	677	13
1169	Inconel	71LiF-29ThF ₄	1000	677	1
1177	Inconel	71LiF-29ThF ₄	1000	677	1.5
1173	Inconel	58NaF-35BeF ₂ -7ThF ₄	1000	677	4
1176	Inconel	58LiF-35BeF ₂ -7ThF ₄	1000	677	1
1234	Inconel	71LiF-16BeF ₂ -13ThF ₄	1000	677	1
9344-2	Inconel	FLiNaK	8760	649	8
9344-2	Inconel	FLiNaK	8735	649	8
1172	Inconel	35LiF-27NaF-38BeF ₂	1000	607	2
1175	Inconel	FLiNaK	1000	607	1
LDRD	INOR-8	FLiNaK	3048	815	0.1
1209	INOR-8	71LiF-29ThF ₄	8760	732	0
1216	INOR-8	58LiF-35BeF ₂ -7ThF ₄	8760	732	1
1240	INOR-8	71LiF-16BeF ₂ -13ThF ₄	8760	732	0
MSRP7	INOR-8	71LiF-16BeF ₂ -13ThF ₄	20000	704	1
MSRP8	INOR-8	58LiF-35BeF ₂ -7ThF ₄	9633	704	0
15A	INOR-8	73LiF-2BeF ₂ -25ThF ₄	39476	677	0.05

Loop #	Alloy	Salt	Duration, h	Peak, °C	Corrosion, mil
1208	INOR-8	FLiNaK	8760	677	1
1190	INOR-8	58NaF-35BeF ₂ -7ThF ₄	8760	677	1
1233	INOR-8	71LiF-16BeF ₂ -13ThF ₄	8760	677	0
1213	INOR-8	71LiF-29ThF ₄	3114	677	0
15	INOR-8	73LiF-2BeF ₂ -25ThF ₄	2003	677	0
1165	INOR-8	FLiNaK	1340	677	0
1164	INOR-8	58NaF-35BeF ₂ -7ThF ₄	1000	677	0
1221	INOR-8	71LiF-29ThF ₄	1000	677	0
1228	INOR-8	71LiF-16BeF ₂ -13ThF ₄	1000	677	0
MSRE	INOR-8	67LiF-33BeF ₂	26000	649	0
9354-3	INOR-8	35LiF-27NaF-38BeF ₂	19942	649	0
1194	INOR-8	FLiNaK	1000	607	0
1195	INOR-8	35LiF-27NaF-28BeF ₂	1000	607	0